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(54) Title: CU-CUO/ZnO<sub>2</sub> CATALYST IN STEAM REFORMING OF METHANOL

(57) Abstract: The present invention relates to a method for the production of hydrogen by a reforming process wherein a catalyst is used which is prepared by a templating technique. Preferably, the catalyst is a CuO and ZnO<sub>2</sub> containing catalyst.

**Cu-CuO/ZrO<sub>2</sub> catalyst in Steam Reforming of Methanol****Description**

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The present invention relates to a method for the production of hydrogen by a reforming process wherein a catalyst is used which is prepared by a templating technique. Preferably, the catalyst is a Cu/CuO and ZrO<sub>2</sub> containing catalyst.

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Using methanol as hydrogen carrier for fuel cell systems is one of the most favourable solutions to supply hydrogen on board in comparison to other hydrocarbon fuels, due to the following main reasons: low temperature in steam-methanol reforming (250°C), high hydrogen to carbon ratio, low CO formation and zero emission of NO<sub>x</sub>, SO<sub>x</sub>. A comparative study of different fuels for on-board hydrogen production for fuel-cell-powered automobiles has been carried out by L.F. Brown [1]. The alternative processes of hydrogen production from methanol are decomposition, steam reforming, partial oxidation and combined reforming of methanol also called oxidative steam reforming of methanol [2-5]. A higher hydrogen content in product stream is obtained in steam reforming compared to partial oxidation and oxidative reforming. Using steam reforming would produce a significantly lower CO content in comparison to decomposition [6] but higher in comparison to oxidative steam reforming [2,4].

25

The commercial catalyst used to generate hydrogen by methanol steam reforming (SRM) process is a copper based catalyst Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. Some preliminary studies on this industrial catalyst have been published recently [2,4,6,7]. Two main problems using this catalyst are the stability of the catalyst activity in time on stream against the temperature and CO formation in product stream, which can deteriorate the Pt electrode and the fuel cell performance, even at a very low concentration [8,9].

30

Investigations on copper catalysts promoted with different metal oxides Cu/Zn [4,10-14], Cu/Cr [4,10,13,15], Cu/Mn [10,16], Cu/Zr [4,13,15,17] have also been done.

- 5 The aim of this work is to synthesise and study copper containing catalysts supported on  $\text{ZrO}_2$  using template technique which show superior properties, stability in time on stream against the temperature and less formation of CO in comparison to the commercial catalyst. The microstructure of precursor and reduced Cu on  $\text{ZrO}_2$  was studied using X-
- 10 ray diffraction and X-ray absorption line profile analysis. The catalyst activity was examined in a fixed reactor and GC was used as an analytical instrument to measure the composition of gas and liquid in the product stream.
- 15 Thus, a first aspect of the present invention is a method for the production of hydrogen by a reforming process wherein a catalyst prepared by a templating technique, preferably a Cu/CuO and  $\text{ZrO}_2$  containing catalyst, is used.
- 20 The method is preferably a steam reforming process which is carried out in a suitable reactor at temperatures which are preferably from about 200 to 300°C. The reactor feed is preferably methanol/ $\text{H}_2\text{O}$  or ethanol/ $\text{H}_2\text{O}$ , more preferably methanol/ $\text{H}_2\text{O}$ .
- 25 The catalyst preferably contains Cu and Zr in a molar ratio from 1:200 to 1:1, more preferably from 1:50 to 1:1. Furthermore, it is preferred that the catalyst contains copper (Cu and CuO) in an amount of from 1 to 50% by weight. Furthermore, it is preferred that the catalyst contains CuO crystallites having an average size of less than 40 Å. These crystallites
- 30 may form from about 1 to about 50% by weight of the total copper content. Furthermore, the catalyst preferably contains metallic copper (Cu) in an amount of about 50 to about 80% of the total copper content. The

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above indicated amounts of CuO crystallites and metallic copper refer to an active catalyst, preferably a catalyst which has been activated by oxidation.

5 The catalyst of the invention is prepared by a templating technique. The templating procedure preferably comprises:

- i) forming an organic polymer in a surfactant solution,
- ii) optionally removing the surfactant,
- 10 iii) coating the organic polymer with Cu compounds and Zr compounds and
- iv) removing organic components by heating.

The organic polymer is an optionally crosslinked acrylate-based polymer which may be formed by free radical polymerization of suitable organic  
15 monomers, e.g. acrylic monomers such as acrylamide, acrylic acid, acrylate esters, glycidylmethacrylate, ethylene glycol dimethacrylate, etc.

The polymer is formed in a surfactant solution. Suitable surfactants are anionic, cationic, non-ionic or zwitterionic surfactants or mixtures thereof,  
20 particularly non-ionic surfactants such as polyoxyethylene containing fatty acid esters and polyethylene glycol ethers. The concentration of the surfactant in the solution is preferably in the range of from 20 to 60 percent by weight.

25 According to step (ii), the surfactant is removed, e.g. by extraction with a suitable solvent, e.g. ethanol.

According to step (iii), the organic polymer is coated with metallic compounds, preferably with Cu compounds and Zr compounds. The  
30 coating is preferably carried out according to a sol-gel process, wherein suitable metal salts and/or hydrolyzable metal compounds are used. Cu compounds are preferably selected from Cu(II) salts with organic or

inorganic acids, e.g. Cu(II) acetyl acetonate, Cu(II) acetate, Cu(II) nitrate and Cu(II) chloride. Zr compounds are preferably selected from hydrolyzable Zr compounds, particularly Zr(IV) compounds, more particularly Zr alkoxides, e.g. Zr(IV) propoxide or Zr(IV) oxy salts, e.g. Zr (IV) oxynitrate and Zr (IV) oxychloride.

The sol-gel procedure comprises contacting the organic polymer with metal compounds in the presence of a hydrolysis solution, whereby a metal sol is hydrolyzed in a hydrolysis solution and deposited on the preformed organic polymer.

Step (iv) comprises removal of organic components, e.g. by heating. For example, heating may be carried out at a temperature from about 420 to about 600°C under suitable conditions. For example, the heating may comprise a two-step procedure, wherein the first step comprises heating in an inert atmosphere, e.g. nitrogen, and subsequently switching the atmosphere to an oxygen containing atmosphere.

In addition to Cu/CuO and ZrO<sub>2</sub>, the catalyst may contain additional components such as Zn, Au, Pd and/or Ni which may be present in oxidic and/or metallic form. The additional components may be present in an amount up to 20% based on the amount of copper on a molar basis.

The CuO and ZrO<sub>2</sub> containing catalyst which is prepared by a templating technique produces less CO in the product stream measured as a function of methanol conversion, compared to a prior art CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.

The Cu-CuO/ZrO<sub>2</sub> catalyst of the invention is almost inactive after reduction. The catalyst activity may be increased by introducing one or several O<sub>2</sub> pulses into the feed, e.g. 50 ml/min oxygen for 5 min. After several O<sub>2</sub> pulses the catalyst reached a maximum and stable activity. This activation procedure seems to be an irreversible process.

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The catalytic activity of the Cu-CuO/ZrO<sub>2</sub> catalyst of the invention is lower than the activity of a comparative commercial catalyst. It is assumed, however, that this low activity is due to the low copper content in the sample of the catalyst of the invention (about 15 wt. %). When plotting the methanol conversion as a function of the mass of copper it was found that the catalyst of the invention is as active as the commercial catalyst.

A comparison of the stability of the catalyst of the invention and the commercial catalyst demonstrated that the methanol conversion is constant in an operation time for higher than 150h. However, the commercial catalyst deactivated monotonically in time.

#### Examples

##### Example 1: Catalyst preparation

For the fabrication of the catalyst a templating procedure was applied. At first a porous polymer gel was formed by free radical polymerization of organic monomers in a highly concentrated surfactant solution [18-21]. This gel was then used as the template in a sol-gel nanocoating process [22,23].

##### 1. a) Materials

The surfactant Tween 60® (T60, polyoxyethylene (20) sorbitan monostearate), the organic monomers acrylamide (AA), glycidylmethacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) as well as the radical initiator potassium persulfate (KPS) were purchased from Aldrich. Zirconium(IV) propoxide (ZrP, 70% in 1-propanol) and copper(II) acetylacetonate (CuAcac<sub>2</sub>) were also obtained from Aldrich. All chemicals were used as received. The water employed during the preparation was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18 MΩ cm.

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## 1. b) Polymer gel preparation

For the preparation of the polymer gel 25.00 g of the structure directing surfactant, T60, were dissolved in 50.00 mL of water. The monomers (6.25 g AA and 6.25 g GMA) were added to this homogenous solution. Upon addition of 2.51 g of EGDMA as a crosslinker, the solution became turbid. The initiator (0.63 g KPS) was dissolved in the mixture, which was then poured into test tubes. Polymerization was carried out at 60°C (at this temperature the solution became clear first before it went opaque due to the formation of the polymer). After 16 hours the gel was taken out of the test tubes and cut into disks. The surfactant was removed by soxhlet extraction (ethanol, 2 days) and subsequent washing with water. Finally the gel was transferred into 2-propanol.

## 1. c) Sol-gel nanocoating

20.0 g ZrP and 2.0 g CuAcac<sub>2</sub> were stirred over night. The resulting dark blue solution is almost saturated with the copper salt. The polymer gels were initially soaked in this solution over night and then in a hydrolysis solution for 24h. The hydrolysis solution was prepared from equal volumes of water and 2-propanol and saturated with CuAcac<sub>2</sub> by stirring it with an excess of the salt for several hours; the undissolved salt was removed by decanting the supersaturated solution. After drying, the polymer gel was removed from the metal oxide by heating the hybrid material over 2 hours to 500°C under a nitrogen atmosphere; then the gas was switched to oxygen and the temperature was maintained for 10 hours.

## Example 2: Catalyst Characterization

The X-ray diffraction (XRD) measurements were performed on a STOE STADI P diffractometer (Cu K $\alpha$  radiation, curved Ge monochromator) in transmission geometry with a curved position sensitive detector.

X-ray absorption spectroscopy (XAS) measurements were performed at beamline X1 at the Hamburg Synchrontron Radiation Laboratory HASYLAB.

The spectra were taken at the Cu K edge in transmission mode using a Si(111) double crystal monochromator. 10 mg of sample were mixed with 30 mg of hexagonal boron nitride and pressed with a force of one ton into a 5 mm diameter self supporting pellet.

The X-ray diffraction pattern of an "as prepared" sample (calcined catalyst precursor) mixed with 50 wt. % corundum as internal standard is shown in Fig. 1. All sample reflections can be identified as belonging to tetragonal (or cubic) zirconia,  $\text{ZrO}_2$ .

Assuming a narrow and uniform distribution, the average domain size can be estimated to be in the order of  $60(\pm 10)$  Å based on the Scherrer formula. By comparison of the peak intensities with the internal standard, the crystallinity of  $\text{ZrO}_2$  is close to 100%, i.e. there is no significant fraction of X-ray amorphous zirconia. The diffractogram yields no peaks belonging to monoclinic  $\text{ZrO}_2$  or any copper containing phase. In addition to the low copper content of the sample, the latter observation can be explained assuming very small crystallites (below 40 Å). Upon reduction of the precursor in 2% hydrogen at 250°C, the XRD pattern changes slightly. In addition to the  $\text{ZrO}_2$  peaks, the strongest reflection of metallic copper (Cu111) becomes barely visible.

The Cu K edge X-ray absorption spectrum of the precursor does not closely resemble the spectra of the copper oxide references (Fig. 2).

However, a restrictive EXAFS fit based on the structure of copper(II) oxide CuO is in very good agreement with the measured data (Fig. 3).

Besides identification of the copper containing phase, the quality of the fit allows us to exclude the presence of other copper phases, including copper incorporated into the  $\text{ZrO}_2$  structure. It turns out that the most important fit parameter is the Debye Waller factor, which adopts rather large values and



causes a strong dampening of the EXAFS amplitudes. Because the spectrum was taken at room temperature, the large Debye Waller factor indicates a significant amount of disorder in the CuO structure and/or very small particle sizes. The latter assumption is in agreement with the fact that CuO was not detected by XRD.

The EXAFS analysis of a reduced sample shows that the reduction of Cu O to Cu is complete within the limit of detection. The structure of the copper metal corresponds to bulk copper except for small particle size.

### Example 3: Catalyst Performance

The measurement of the steam reforming reaction was carried out at atmospheric pressure in a tubular stainless steel reactor (10 mm i.d.). In order to study the kinetic properties of more than one catalyst at once, three of these reactors were placed into an aluminium heating block for the heat transfer as can be seen in the experimental setup illustrated in Fig. 4. Six cartridge heaters of 125 watt each were put inside the aluminium block. The temperature of the reactor was regulated by an electronic controller which powers the cartridge heaters. Thermocouple was used as a reference. The temperature of the catalyst bed was monitored by the second thermocouple placed inside the catalyst bed. In order to obtain the same liquid flow rate for all the reactors, three stainless steel capillaries of the same diameter and length were placed between the HPLC-pump and the inlet of the reactor. The advantages using this three channels reactor to study the kinetic properties of the catalyst: direct comparison of three catalyst's measurements in the same reaction conditions, possibly catalyst change during the measurement, availability of using different gases. The catalyst was supported by a fixed fine mesh grid. For the flow conditioning inert Pyrex beads of the catalyst's size (0.85 - 1.0mm) were placed on top and below the catalyst bed. The catalyst in the form of powder was first diluted with five times weight amount of boron nitride, then the mixture was pressed, ground and sieved to get a defined particle size. The

reactants, water and methanol, were introduced into the reactor in a molar ratio of 1 and at a liquid flow rate of 0.07 ml/min.

Prior to the activity measurement, the catalyst was reduced at 250°C with the reaction mixture. By passage through a series of cool traps, non condensable gases were separated from the liquid. The dry effluent gases were analysed on a 25.0m x 0.53mm CarboPLOT P7 column using a Varian GC 3800 equipped with a thermal conductivity detector (TCD). Helium was used as carrier gas. The composition of the condensed mixture that contained mostly methanol and water was analysed by a second gas Chromatography Intersmat IGC 120ml on a 50m x 0.53mm fused Silica PLOT CP-Wax 58 (FFAP).

In order to compare the activity and selectivity behaviour of the Cu/ZrO<sub>2</sub>, a commercial catalyst for the methanol synthesis Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (Cu content approx. 50 wt. %) was examined at the same reaction conditions.

### 3. a) Catalytic Activity

The experiment in Fig. 4(a) shows methanol conversion as a function of  $W_{cat}/F_m$  ratio at 250°C ( $W_{cat}$ : mass of catalyst [kg],  $F_m$ : molar flow rate of methanol [mmol/s]). The variation of the contact time was carried out by changing the liquid flow rate of the methanol water mixture from 0.02 to 0.2 ml/min.

The curve (methanol conversion vs.  $W_{cat}/F_m$ , measured over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst) is comparable to those found in the literature [2,16]. The activity of the Cu/ZrO<sub>2</sub> catalyst is significantly lower than that of the commercial catalyst. This is due to the low copper content in the Cu/ZrO<sub>2</sub> sample (about 15 wt. %). In Fig. 4(b), the methanol conversion is plotted as a function of  $W_{Cu}/F_m$  with  $W_{Cu}$  indicating the mass of the copper. The results show that the CuO/ZrO<sub>2</sub> catalyst is as active as the commercial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.

- 10 -

## 3. b) CO formation

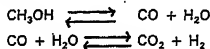
The CO formation in the product stream of the methanol-steam reforming process is a crucial point concerning CO absorption on the Pt-electrode, which can deteriorate the polymer electrolyte fuel cell performance.

Generally, it is known that CO concentration increases with increasing of the reaction temperature and increasing of methanol conversion resp. long contact time. As reported in the literature, the essential ways to suspend the CO formation in the steam reforming process are:

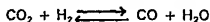
1. increasing the water to methanol ratio in the feed [2,6,25]
2. addition of oxygen into the process [2,4]

The suggestions in the literature concerning the CO formation in the methanol-steam reforming process can generally be divided as follows:

1. CO is obtained as an intermediate product, formed by decomposition of methanol and followed by water gas shift reaction [26,27]



2. CO formed in a consecutive reaction i.e. reverse water gas reaction [2,17]



The experimental result, CO concentration as a function of  $W_{\text{cat}}/F_m$  ratio over CuO/ZrO<sub>2</sub> catalyst is plotted in Fig. 5. CO concentration, measured as volume content in the dry product stream, increased with increasing of the  $W_{\text{cat}}/F_m$  ratio for all temperatures. The dependence of CO concentration on the  $W_{\text{cat}}/F_m$  ratio resp. the contact time for all temperatures seems to form the S-shaped curve. These results indicate that CO is formed as a consecutive product by reverse water-gas shift reaction.

It also shows that the CO concentration increases with increasing reaction temperatures at constant contact time.

CO concentration as a function of methanol conversion over the  $\text{CuO/ZrO}_2$  catalyst and the  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst is displayed in Fig. 6. The exponential increasing of CO formation with the increasing of methanol conversion is observed for both catalysts. The increasing of CO formation becomes very significant at a high methanol conversion. The process of methanol steam reforming produces less CO over the  $\text{CuO/ZrO}_2$  catalyst compared to the  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst. These results corroborate those reported in the literature. Though the  $\text{CuO/ZrO}_2$  catalyst is less active than the  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst, a lower CO content is obtained in the product stream [4] in the former case.

#### Example 4: Stability of the Catalyst

One of the main problems using the commercial  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst in the methanol-steam reforming process is the deactivation in time on stream. The experiment presented in Fig. 7 shows the methanol conversion as a function of the operation time, carried out over the  $\text{Cu/ZrO}_2$  catalyst and the  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst. In order to compare the stability of both catalysts in time on stream, the measurement was carried out at similar reaction conditions, i.e. dilution of the catalyst with inert material, loading of the catalyst in the reactor.

The result shows that the deactivation behaviour of the  $\text{CuO/ZrO}_2$  catalyst looks similar to those of the  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst. The deactivation of the catalyst in time on stream can be divided into two sections, (i) 0-100h, the methanol conversion decreasing exponentially, (ii) > 100h linearly. The difference of both curves was determined at the time on stream more than 150h. The measurement on the  $\text{CuO/ZrO}_2$  catalyst demonstrated that the methanol conversion is constant in the operation time for higher than 150h. However, the  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst deactivated monotonically in time on stream more than 150h.

## Claims

1. A method for the production of hydrogen by a reforming process  
5 wherein a Cu/CuO and ZrO<sub>2</sub> containing catalyst prepared by a templating technique is used.
2. The method of claim 1 wherein the reforming process is a steam reforming process.
- 10 3. The method of claims 1 or 2 wherein the catalyst contains Cu and Zr in a molar ratio of from 1:200 to 1:1.
4. The method of any one of claims 1 to 3 wherein the catalyst  
15 contains copper in an amount of from 1 to 50 percent by weight.
5. The method of any one of claims 1 to 4 wherein the catalyst contains CuO crystallites having an average size of less than 40 Å.
- 20 6. The method of any one of claims 1 to 5 wherein the catalyst contains metallic copper in an amount of 50 to 80 percent of the total copper content.
7. The method of any one of claims 1 to 6 wherein the templating  
25 procedure comprises:
  - i) forming an organic polymer in a surfactant solution,
  - ii) optionally removing the surfactant,
  - iii) coating the organic polymer with Cu compounds and Zr compounds and
  - 30 iv) removing organic components by heating.

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8. The method of claim 7 wherein the organic polymer is an optionally crosslinked acrylate-based polymer.
9. The method of claims 7 or 8 wherein the surfactant is a polyoxyethylene containing fatty acid ester or a polyoxyethylene ether.
10. The method of any one of claims 7 to 9 wherein the organic polymer is formed by free radical polymerization.
11. The method of any one of claims 7 to 10 wherein the Cu compounds are selected from organic or inorganic Cu(II) salts, e.g. Cu(II) acetylacetonate, Cu(II) acetate, Cu(II) nitrate and Cu(II) chloride.
12. The method of any one of claims 7 to 11 wherein the Zr compounds are selected from hydrolyzable Zr compounds, particularly Zr(IV) alkoxides, e.g. Zr(IV) propoxide or Zr(IV) oxy salts, e.g. Zr(IV) oxy nitrate and Zr(IV) oxychloride.
13. The method of any one of claims 7 to 12 wherein the heating comprises a first heating step in an inert atmosphere and a second heating step in an oxygen containing atmosphere.
14. The method of any one of claims 7 to 13 wherein the heating temperature is from 420 to 600°C.
15. The method of any one of claims 1-14 comprising activating the catalyst by oxidation.
16. Cu/CuO and ZrO<sub>2</sub> containing catalyst prepared by a templating technique.

17. The catalyst of claim 16 which has been activated by oxidation.

Figure 1

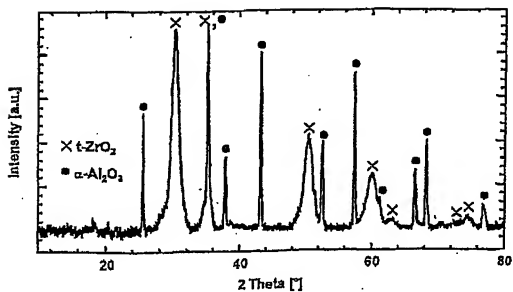


Fig. 1 X-ray diffraction pattern of a calcined catalyst precursor (CuO/ZrO<sub>2</sub>) mixed with 50 wt. % corundum as internal standard.



Figure 2

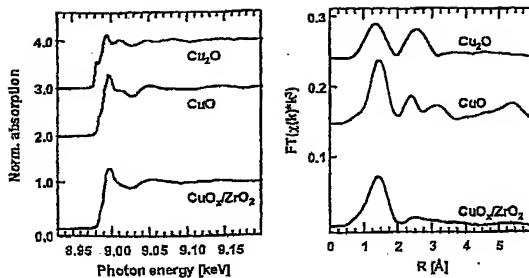
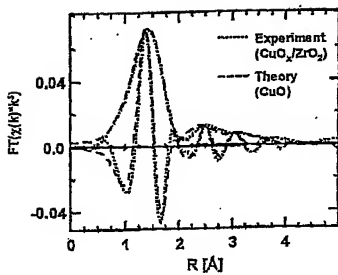


Fig. 2 Cu K-edge X-ray absorption spectrum of the catalyst precursor (CuO/ZrO<sub>2</sub>)

-3/7-

Figure 3

Fig. 3 EXAFS fit to an experimental data of copper(II) oxide (CuO/ZrO<sub>2</sub>)

-4/7-

Figure 4(a)

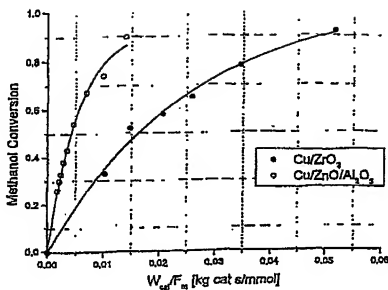


Fig. 4(a) Comparison of activity between CuO/ZrO<sub>2</sub> catalyst and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. Methanol conversion vs.  $W_{cat}/F_m$  ratio ( $W_{cat}$ : mass of catalyst,  $F_m$ : molar flow rate of methanol).

Figure 4(b)

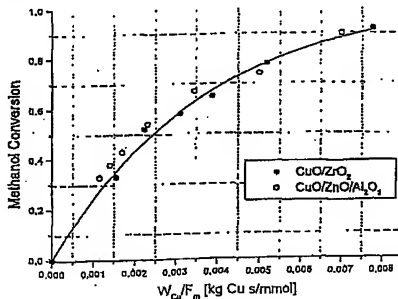


Fig. 4(b) Comparison of activity between CuO/ZrO<sub>2</sub> catalyst and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. Methanol conversion vs.  $W_{cat}/F_m$  ratio ( $W_{cat}$ : mass of copper).

Figure 5

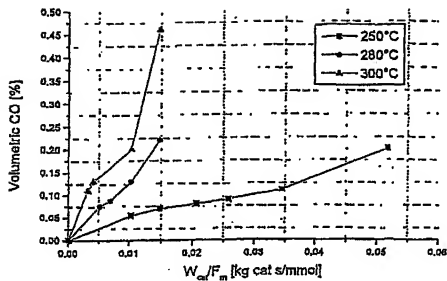


Fig. 5 CO concentration as a function of  $W_{cat}/F_m$  ratio. Mass of the catalyst ( $CuO/ZrO_2$ ) = 300mg.

-6/7-

Figure 6

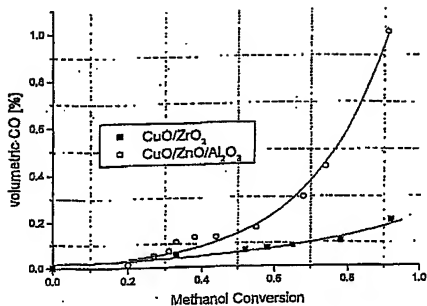


Fig. 6 CO concentration in dependence on methanol conversion at 250°C.

Figure 7

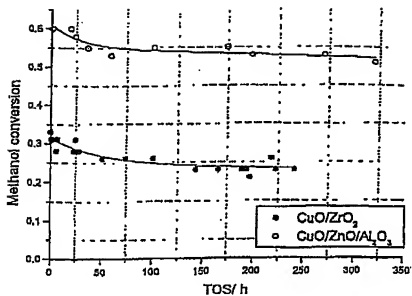


Fig. 7 Deactivation experiment with CuO/ZrO<sub>2</sub> catalyst and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst at comparable reaction conditions.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP2004/002765

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C01B3/32 B01J23/72 B01J37/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELD OF SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, MPI Data, PAJ, CHEM ABS Data, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LINDSTROM B ET AL: "Steam reforming of methanol over copper-based monoliths: the effects of zirconia doping" JOURNAL OF POWER SOURCES, ELSEVIER SEQUOIA S.A. LAUSANNE, CH, vol. 106, no. 1-2, 1 April 2002 (2002-04-01), pages 264-273, XP004348698 ISSN: 0378-7753	1-6, 15-17
A	p. 266-273 "Experimental", "Results", "Conclusions"	7-14
A	EP 1 077 081 A (MITSUBISHI HEAVY IND LTD) 21 February 2001 (2001-02-21) claims 1-3, 5, 10 paragraphs '0008! - '0025!, '0027! - '0033!, '0041! examples	1-17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

29 July 2004

Date of mailing of the international search report

10/08/2004

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## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP2004/002765

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 904 913 A (STEINWANDEL JUERGEN ET AL) 18 May 1999 (1999-05-18) claim 1 column 1, line 62 - column 2, line 14	1-17
A	KAPOOR M P ET AL: "Methanol decomposition over palladium supported mesoporous CeO <sub>2</sub> -ZrO <sub>2</sub> mixed oxides" MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 44-45, 6 April 2001 (2001-04-06), pages 565-572, XP004247192 ISSN: 1387-1811 p.566-571 "Experimental", "Results and Discussion", "Conclusions"	1-17
T	H. PURNAMA, F. GIRGSDIES, T. RESSLER, J.H. SCHATTKA, R.A. CARUSO, R. SCHONÄCKER, R. SCHLÖGL: "Activity and selectivity of a nanostructured CuO/ZrO <sub>2</sub> catalyst in the steam reforming of methanol" CATALYSIS LETTERS, vol. 94, no. 1-2, April 2004 (2004-04), pages 61-68, XP001194604 the whole document	1-17

Form PCT/ISA/210 (continuation of second sheet) (January 2004)



## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP2004/002765

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			CA 2315495 A1	11-02-2001
			EP 1077081 A2	21-02-2001
			US 6576217 B1	10-06-2003
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